

Claims

1. A method for monitoring a reverse osmosis membrane separation process including a reverse osmosis membrane capable of separating a feed stream into a first stream and a second stream to remove solutes from the feed stream comprising the steps of:

providing an inert fluorescent tracer and a tagged fluorescent agent;

introducing the inert fluorescent tracer and tagged fluorescent agent into the feed stream;

providing a fluorometer to detect the fluorescent signal of the inert fluorescent tracer and the tagged fluorescent agent in at least one of the feed stream, the first stream and the second stream; and

using the fluorometer to determine an amount of the inert fluorescent tracer and the tagged fluorescent agent in at least one of the feed stream, the first stream and the second stream.

2. The method of claim 1 further comprising the step of evaluating at least one process parameter specific to the reverse osmosis membrane separation process based on the amount of the inert fluorescent tracer and the tagged fluorescent agent that are measured.

3. The method of claim 1 wherein the reverse osmosis membrane is selected from the group consisting of hollow fiber membrane elements, tubular membrane elements, spiral-wound membrane elements, plate and frame membrane elements and combinations thereof.

4. The method of claim 3 wherein the reverse osmosis membrane is a hollow fiber membrane.

5. The method of claim 3 wherein the reverse osmosis membrane is a tubular membrane.

6. The method of claim 1 wherein the inert fluorescent tracer is selected from the group consisting of 3,6-acridinediamine, N,N,N',N'-tetramethyl-,monohydrochloride; 2-anthracenesulfonic acid sodium salt; 1,5-anthracenedisulfonic acid; 2,6-anthracenedisulfonic acid; 1,8-anthracenedisulfonic acid; anthra[9,1,2-cde]benzo[rst]pentaphene-5,10-diol, 16,17-dimethoxy-,bis(hydrogen sulfate), disodium salt; bathophenanthrolinedisulfonic acid disodium salt; amino 2,5-benzene disulfonic acid; 2-(4-aminophenyl)-6-methylbenzothiazole; 1H-benz[de]isoquinoline-5-sulfonic acid, 6-amino-2,3-dihydro-2-(4-methylphenyl)-1,3-dioxo-, monosodium salt; phenoxazin-5-ium, 1-(aminocarbonyl)-7-(diethylamino)-3,4-dihydroxy-, chloride; benzo[a]phenoxazin-7-ium, 5,9-diamino-,acetate; 4-dibenzofuransulfonic acid; 3-dibenzofuransulfonic acid; 1-ethylquinaldinium iodide; fluorescein; fluorescein, sodium salt; Keyfluor White ST; benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis[5-[[4-[bis(2-hydroxyethyl)amino]-6-[(4-sulfophenyl)amino]-1,3,5-triazin-2-yl]amino]-,tetrasodium salt; C.I. Florescent Brightener 230; benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis[5-[[4-[bis(2-hydroxyethyl)amino]-6-[(4-sulfophenyl)amino]-1,3,5-triazin-2-yl]amino]-,tetrasodium salt; 9,9'-biacridinium, 10,10'-dimethyl-, dinitrate; 1-deoxy-1-(3,4-dihydro-7,8-dimethyl-2,4-dioxobenzo[g]pteridin-10(2H)-yl)- ribitol; mono-, di-, or tri-sulfonated naphthalenes selected from the group consisting of 1,5-naphthalenedisulfonic acid, disodium salt (hydrate); 2-amino-1-naphthalenesulfonic acid; 5-amino-2-naphthalenesulfonic acid; 4-amino-3-hydroxy-1-naphthalenesulfonic acid; 6-amino-4-hydroxy-2-naphthalenesulfonic acid; 7-amino-1,3-naphthalenesulfonic acid, potassium salt; 4-amino-5-hydroxy-2,7-naphthalenedisulfonic acid; 5-dimethylamino-1-naphthalenesulfonic acid; 1-amino-4-naphthalene sulfonic acid; 1-amino-7-naphthalene sulfonic acid; and 2,6-naphthalenedicarboxylic acid, dipotassium salt; 3,4,9,10-perylenetetracarboxylic acid; C.I. Fluorescent Brightener 191; C.I. Fluorescent Brightener 200;

benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis[5-(4-phenyl-2H-1,2,3-triazol-2-yl)-, dipotassium salt; benzenesulfonic acid, 5-(2H-naphtho[1,2-d]triazol-2-yl)-2(2-phenylethenyl)-, sodium salt; 1,3,6,8-pyrenetetrasulfonic acid, tetrasodium salt; pyranine; quinoline; 3H-phenoxazin-3-one, 7-hydroxy-, 10-oxide; xanthylium, 9-(2,4-dicarboxyphenyl)-3,6-bis(diethylamino)-, chloride, disodium salt; phenazinium, 3,7-diamino-2,8-dimethyl-5-phenyl-, chloride; C.I. Fluorescent Brightener 235; benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis[5-[[4-[bis(2-hydroxyethyl)amino]-6-[(4-sulfophenyl)amino]-1,3,5-triazin-2-yl]amino]-, tetrasodium salt; benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis[5-[[4-[(2-hydroxypropyl)amino]-6-(phenylamino)-1,3,5-triazin-2-yl]amino]-, disodium salt; xanthylium, 3,6-bis(diethylamino)-9-(2,4-disulfophenyl)-, inner salt, sodium salt; benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis[5-[[4-[(aminomethyl)(2-hydroxyethyl)amino]-6-(phenylamino)-1,3,5-triazin-2-yl]amino]-, disodium salt; Tinopol DCS; benzenesulfonic acid, 2,2'-([1,1'-biphenyl]-4,4'-diyldi-2,1-ethenediyl)bis, disodium salt; benzenesulfonic acid, 5-(2H-naphtho[1,2-d]triazol-2-yl)-2-(2-phenylethenyl)-, sodium salt; 7-benzothiazolesulfonic acid, 2,2'-(1-triazene-1,3-diyldi-4,1-phenylene)bis[6-methyl-, disodium salt; and all ammonium, potassium and sodium salts thereof; and all mixtures thereof.

7. The method of claim 1 wherein the inert fluorescent tracer is selected from the group consisting of 1-deoxy-1-(3,4-dihydro-7,8-dimethyl-2,4-dioxobenzo[g]pteridin-10(2H)-yl)-D ribitol; fluorescein; fluorescein, sodium salt; 2-anthracenesulfonic acid sodium salt; 1,5-anthracenedisulfonic acid; 2,6-anthracenedisulfonic acid; 1,8-anthracenedisulfonic acid; mono-, di-, or tri-sulfonated naphthalenes selected from the group consisting of 1,5-naphthalenedisulfonic acid, disodium salt (hydrate); 2-amino-1-naphthalenesulfonic acid; 5-amino-2-

naphthalenesulfonic acid; 4-amino-3-hydroxy-1-naphthalenesulfonic acid; 6-amino-4-hydroxy-2-naphthalenesulfonic acid; 7-amino-1,3-naphthalenesulfonic acid, potassium salt; 4-amino-5-hydroxy-2,7-naphthalenedisulfonic acid; 5-dimethylamino-1-naphthalenesulfonic acid; 1-amino-4-naphthalene sulfonic acid; 1-amino-7-naphthalene sulfonic acid; and 2,6-naphthalenedicarboxylic acid, dipotassium salt; 3,4,9,10-perylenetetracarboxylic acid; C.I. Fluorescent Brightener 191; C.I. Fluorescent Brightener 200; benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis[5-(4-phenyl-2H-1,2,3-triazol-2-yl)-, dipotassium salt; benzenesulfonic acid, 5-(2H-naphtho[1,2-d]triazol-2-yl)-2-(2-phenylethenyl)-, sodium salt; 1,3,6,8-pyrenetetrasulfonic acid, tetrasodium salt; pyranine; quinoline; 3H-phenoxazin-3-one, 7-hydroxy-, 10-oxide; xanthylum, 9-(2,4-dicarboxyphenyl)-3,6-bis(diethylamino)-, chloride, disodium salt; phenazinium, 3,7-diamino-2,8-dimethyl-5-phenyl-, chloride; C.I. Fluorescent Brightener 235; benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis[5-[[4-[bis(2-hydroxyethyl)amino]-6-[(4-sulfophenyl)amino]-1,3,5-triazin-2-yl]amino]-, tetrasodium salt; benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis[5-[[4-[2-hydroxypropyl]amino]-6-(phenylamino)-1,3,5-triazin-2-yl]amino]-, disodium salt; xanthylum, 3,6-bis(diethylamino)-9-(2,4-disulfophenyl)-, inner salt, sodium salt; benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis[5-[[4-[(aminomethyl)(2-hydroxyethyl)amino]-6-(phenylamino)-1,3,5-triazin-2-yl]amino]-, disodium salt; Tinopol DCS; benzenesulfonic acid, 2,2'-([1,1'-biphenyl]-4,4'-diyl)-2,1-ethenediyl)bis-, disodium salt; benzenesulfonic acid, 5-(2H-naphtho[1,2-d]triazol-2-yl)-2-(2-phenylethenyl)-, sodium salt; 7-benzothiazolesulfonic acid, 2,2'-(1-triazene-1,3-diyl)-4,1-phenylene)bis[6-methyl-, disodium salt; and all ammonium, potassium and sodium salts thereof; and all mixtures thereof.

8. The method of claim 1 wherein the inert fluorescent tracer is selected from the group consisting of 1,3,6,8-pyrenetetrasulfonic acid tetrasodium salt; 1,5-naphthalenedisulfonic

acid disodium salt (hydrate); xanthylium, 9-(2,4-dicarboxyphenyl)-3,6-bis(diethylamino)-, chloride, disodium salt; 1-deoxy-1-(3,4-dihydro-7,8-dimethyl-2,4-dioxobenzo[g]pteridin-10(2H)-yl) – D-ribitol; fluorescein; fluoroescien, sodium salt; 2-anthracenesulfonic acid sodium salt; 1,5-anthracenedisulfonic acid; 2,6-anthracenedisulfonic acid; 1,8-anthracenedisulfonic acid; and mixtures thereof.

9. The method of claim 1 wherein the tagged fluorescent agent comprises a water-soluble polymer tagged with at least one fluorescent group.

10. The method of claim 9 wherein the fluorescent group is selected from the group consisting of hydroxy allyloxypropyl naphthalimide quat, 4-methoxy-N-(3-N'N'-dimethylaminopropyl) naphthalimide, 2 hydroxy-3-allyloxypropyl quat, 8-(3-vinylbenzyloxy)-1, 3, 6-pyrene trisulfonic acid; 8-(4-vinylbenzyloxy)-1,3,6-pyrene trisulfonic acid, 8-(allyloxy)-1,3,6-pyrene trisulfonic acid, 1-(substituted) naphthalene, 9-(substituted) anthracene, 2-(substituted) quinoline monohydrochloride, 2-(substituted) benzimidazole, 5-(substituted) fluorescein, 4-(substituted) coumarin, coumarin derivatives, 3-(substituted)-6, 7-dimethoxy-1-methyl-2(1H)-quinoxazolinone, mixtures thereof and derivatives thereof.

11. The method of claim 9 wherein the water-soluble polymer comprises a monomer selected from the group consisting of acrylamide, acrylic acid, methacrylamide, vinyl acetate, dimethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl acrylate benzyl chloride quaternary salt, diallyldimethyl ammonium chloride, N-vinyl formamide; dimethylaminoethyl methacrylate methyl chloride quaternary salt, dimethylaminoethyl

methacrylate benzyl chloride quaternary salt, methacrylamino propyl trimethyl ammonium chloride, acrylamidopropyl trimethyl ammonium chloride, and combinations thereof.

5 12. The method of claim 1 wherein the tagged fluorescent agent comprises a
copolymer of acrylate and acrylamide tagged with a hydroxy allyloxypropyl naphthalimide quat in
an amount of about 2% or less by weight of the copolymer.

 13. The method of claim 1 wherein the inert fluorescent tracer and the tagged
10 fluorescent agent are each introduced into the feed stream in an amount from about 5 ppt to
about 1000 ppm.

 14. The method of claim 1 wherein the inert fluorescent tracer and the tagged
fluorescent agent are each introduced into the feed stream in an amount from about 1 ppb to
15 about 50 ppm.

 15. The method of claim 1 wherein the inert fluorescent tracer and the tagged
fluorescent agent are each introduced into the feed stream in an amount from about 5 ppb to
about 50 ppb.

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 16. The method of claim 1 wherein the inert fluorescent tracer and tagged fluorescent
agent are added to a formulation capable of treating scaling and/or fouling prior to addition to the
feed stream.

17. A method for monitoring a reverse osmosis membrane separation system of a water purification process comprising the steps of

- a) providing a reverse osmosis membrane capable of removing solutes from a feed stream suitable for use in an industrial process comprising the steps of:
- b) adding an inert fluorescent tracer and a tagged fluorescent agent to the feed stream
- c) contacting the reverse osmosis membrane with the feed stream;
- d) separating the feed stream into a permeate stream and a concentrate stream to remove solutes from the feed stream
- e) providing a fluorometer to detect the fluorescent signal of the inert fluorescent tracer and the tagged fluorescent agent in at least one of the feed stream, the permeate stream and the concentrate stream;
- f) using the fluorometer to measure an amount of the inert fluorescent tracer and the tagged fluorescent agent in at least one of the feed stream, the permeate stream and the concentrate stream; an
- g) determining a ratio of the inert fluorescent tracer to the tagged fluorescent agent based on the measurable amounts of the inert fluorescent tracer and the tagged fluorescent agent.

18. The method of claim 17 further comprising the step of evaluating the removal of solutes from the feed stream based on the ratio.

19. The method of claim 17 wherein the industrial process is selected from the group consisting of raw water processes, waste water processes, industrial water processes, municipal

water treatment, food and beverage processes, pharmaceutical processes, electronic manufacturing, utility operations, pulp and paper processes, mining and mineral processes, transportation-related processes, textile processes, plating and metal working processes, laundry and cleaning processing, leather and tanning processes, and paint processes.

20. The method of claim 17 wherein the feed stream contacts the reverse osmosis membrane in at least one of a cross-flow and a perpendicular flow relative to the reverse osmosis membrane to remove solutes from the feed stream.

21. The method of claim 17 wherein the inert fluorescent tracer is selected from the group consisting of 3,6-acridinediamine, N,N,N',N'-tetramethyl-,monohydrochloride; 2-anthracenesulfonic acid sodium salt; 1,5-anthracenedisulfonic acid; 2,6-anthracenedisulfonic acid; 1,8-anthracenedisulfonic acid; anthra[9,1,2-cde]benzo[rst]pentaphene-5,10-diol, 16,17-dimethoxy-,bis(hydrogen sulfate), disodium salt; bathophenanthrolinedisulfonic acid disodium salt; amino 2,5-benzene disulfonic acid; 2-(4-aminophenyl)-6-methylbenzothiazole; 1H-benz[de]isoquinoline-5-sulfonic acid, 6-amino-2,3-dihydro-2-(4-methylphenyl)-1,3-dioxo-, monosodium salt; phenoxazin-5-ium, 1-(aminocarbonyl)-7-(diethylamino)-3,4-dihydroxy-, chloride; benzo[a]phenoxazin-7-ium, 5,9-diamino-,acetate; 4-dibenzofuransulfonic acid; 3-dibenzofuransulfonic acid; 1-ethylquinaldinium iodide; fluorescein; fluorescein, sodium salt; Keyfluor White ST; benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis[5-[[4-[bis(2-hydroxyethyl)amino]-6-[(4-sulfophenyl)amino]-1,3,5-triazin-2-yl]amino]-,tetrasodium salt; C.I. Florescent Brightener 230; benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis[5-[[4-[bis(2-hydroxyethyl)amino]-6-[(4-sulfophenyl)amino]-1,3,5-triazin-2-yl]amino]-,tetrasodium salt; 9,9'-

biacridinium, 10,10'-dimethyl-, dinitrate; 1-deoxy-1-(3,4-dihydro-7,8-dimethyl-2,4-dioxobenzo[g]pteridin-10(2H)-yl)- ribitol; mono-, di-, or tri-sulfonated naphthalenes selected from the group consisting of 1,5-naphthalenedisulfonic acid, disodium salt (hydrate); 2-amino-1-naphthalenesulfonic acid; 5-amino-2-naphthalenesulfonic acid; 4-amino-3-hydroxy-1-naphthalenesulfonic acid; 6-amino-4-hydroxy-2-naphthalenesulfonic acid; 7-amino-1,3-naphthalenesulfonic acid, potassium salt; 4-amino-5-hydroxy-2,7-naphthalenedisulfonic acid; 5-dimethylamino-1-naphthalenesulfonic acid; 1-amino-4-naphthalene sulfonic acid; 1-amino-7-naphthalene sulfonic acid; and 2,6-naphthalenedicarboxylic acid, dipotassium salt; 3,4,9,10-perylenetetracarboxylic acid; C.I. Fluorescent Brightener 191; C.I. Fluorescent Brightener 200; benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis[5-(4-phenyl-2H-1,2,3-triazol-2-yl)-, dipotassium salt; benzenesulfonic acid, 5-(2H-naphtho[1,2-d]triazol-2-yl)-2-(2-phenylethenyl)-, sodium salt; 1,3,6,8-pyrenetetrasulfonic acid, tetrasodium salt; pyranine; quinoline; 3H-phenoxazin-3-one, 7-hydroxy-, 10-oxide; xanthylum, 9-(2,4-dicarboxyphenyl)-3,6-bis(diethylamino)-, chloride, disodium salt; phenazinium, 3,7-diamino-2,8-dimethyl-5-phenyl-, chloride; C.I. Fluorescent Brightener 235; benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis[5-[[4-[bis(2-hydroxyethyl)amino]-6-[(4-sulfophenyl)amino]-1,3,5-triazin-2-yl]amino]-, tetrasodium salt; benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis[5-[[4-[(2-hydroxypropyl)amino]-6-(phenylamino)-1,3,5-triazin-2-yl]amino]-, disodium salt; xanthylum, 3,6-bis(diethylamino)-9-(2,4-disulfophenyl)-, inner salt, sodium salt; benzenesulfonic acid, 2,2'-(1,2-ethenediyl)bis[5-[[4-[(aminomethyl)(2-hydroxyethyl)amino]-6-(phenylamino)-1,3,5-triazin-2-yl]amino]-, disodium salt; Tinopol DCS; benzenesulfonic acid, 2,2'-([1,1'-biphenyl]-4,4'-diyl-di-2,1-ethenediyl)bis-, disodium salt; benzenesulfonic acid, 5-(2H-naphtho[1,2-d]triazol-2-yl)-2-(2-phenylethenyl)-, sodium salt; 7-benzothiazolesulfonic acid, 2,2'-(1-triazene-1,3-diyl-di-4,1-phenylene)bis[6-

methyl-, disodium salt; and all ammonium, potassium and sodium salts thereof; and all mixtures thereof.

5 22. The method of claim 17 wherein the tagged fluorescent agent comprises a
polymeric water-soluble compound tagged with at least one fluorescent group selected from the
group consisting of hydroxy allyloxypropyl naphthalimide quat, 4-methoxy-N-(3-N'N'-
dimethylaminopropyl) naphthalimide, 2 hydroxy-3-allyloxypropyl quat, 8-(3-vinylbenzyloxy)-1,
3, 6-pyrene trisulfonic acid; 8-(4-vinylbenzyloxy)-1,3,6-pyrene trisulfonic acid, 8-(allyloxy)-
10 1,3,6-pyrene trisulfonic acid, 1-(substituted) naphthalene, 9-(substituted) anthracene, 2-
(substituted) quinoline monohydrochloride, 2-(substituted) benzimidazole, 5-(substituted)
fluorescein, 4-(substituted) coumarin, coumarin derivatives, 3-(substituted)-6, 7-dimethoxy-1-
methyl-2(1H)-quinoxazolinone, mixtures thereof and derivatives thereof.

15 23. A reverse osmosis membrane separation system capable of purifying a feed
stream suitable for use in an industrial process comprising:
a reverse osmosis membrane capable of separating the feed stream containing an inert
fluorescent tracer and a tagged fluorescent agent into a permeate stream and a concentrate stream
20 to remove one or more solutes from the feed stream;
a detection device capable of fluorometrically measuring an amount of the inert
fluorescent tracer and the tagged fluorescent agent each ranging from about 5 ppt to about
1000 ppm in at least one of the feed stream, the permeate stream and the concentrate stream

wherein the detection device is capable of producing a signal indicative of the amount of inert fluorescent tracer and tagged fluorescent agent that is measured; and

5 a controller capable of processing the signal to monitor and/or control the purification of the feed stream.

24. The method of claim 23 wherein the reverse osmosis membrane separation system is capable of evaluating at least one process parameter specific to reverse osmosis membrane separation
10 selected from the group consisting of operational parameters, chemical parameters, a ratio of the inert fluorescent tracer to the tagged fluorescent agent, mechanical parameters and combinations thereof.

25. The method of claim 23 wherein the controller is capable of controllably adjusting
15 an amount of treatment agents added to the feed stream in order to treat scaling and/or fouling during reverse osmosis membrane separation.

26. A method for monitoring and controlling a reverse osmosis membrane separation process including a reverse osmosis membrane capable of removing solutes from a feed stream
20 for use in an industrial process comprising the steps of:

adding an inert fluorescent tracer and a tagged fluorescent agent to the feed stream;
contacting the reverse osmosis membrane with the feed stream;
separating the feed stream into a first effluent stream and a second effluent stream to remove solutes from the feed stream;

providing a fluorometer to detect the fluorescent signal of the inert fluorescent tracer and the tagged fluorescent agent in at least one of the feed stream, the first effluent stream and the second effluent stream;

5 using the fluorometer to measure the inert fluorescent tracer and the tagged fluorescent agent in an amount ranging from about 5 ppt to about 1000 ppm in at least one of the feed stream, the first effluent stream and the second effluent stream; and

 evaluating at least one process parameter specific to reverse osmosis membrane separation based on the measurable amounts of the inert fluorescent tracer and the tagged
10 fluorescent agent.

27. The method of claim 26 wherein the process parameters are selected from the group consisting of operational parameters, chemical parameters, a ratio of the inert fluorescent tracer to the tagged fluorescent agent, mechanical parameters and combinations thereof.

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28. The method of claim 27 comprising controllably and responsively adjusting at least one process parameter to enhance performance during reverse osmosis membrane separation.

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29. The method of claim 26 comprising monitoring and controlling a treatment agent added to the reverse osmosis membrane separation process in order to treat scaling and/or fouling.